FOOD AND ANIMAL FEED CONTAMINATION BY PCDDs-PCDFs IN ITALY IN YEAR 2001

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), collectively referred as to dioxins are ubiquitous toxic contaminants mainly originating from thermal and incineration processes and representing a potential risk for human health. In Italy PCDDs and PCDFs monitoring has been introduced in the National Residues Surveillance Plan (NRSP) since 1999 and all relevant laboratory tests have been carried out at the Istituto Zooprofilattico Sperimentale dell'Abruzzo e del Molise (ISO/IEC 17025 accredited), following designation by the Ministry of Health[1].

The aim of this study was to evaluate dioxin contamination trends in food of animal origin and in animal feed by a comparison of PCDD/Fs levels obtained in the present survey with those of the national monitoring plan conducted in the period 1999-2000 and reported in a previous paper[2].

Materials and methods

According to 2001 NRSP sampling plan, a total of 250 samples (see Table 1 for details) were collected by the regional veterinary services, covering the national territory. All samples were homogenized and a representative aliquot of sample was mixed to diatomaceous earth and spiked with PCDD/Fs standard solution, containing ^{13}C-labelled 2,3,7,8-congeners (Wellington Laboratories). Fat extraction was performed by accelerated solvent extraction (ASE) using a Dionex ASE 200 instrument with a mixture of n-hexane/acetone 80:20 (v/v). The collected extract was evaporated to dryness in a Zymark Turbovap evaporation system and the fat residue was weighed. Milk samples were first added of ethyl alcohol in a separatory funnel in order to precipitate proteins, and then fat was extracted by using a mixture of diethyl ether/petroleum ether 1:1 (v/v). The extract was taken to dryness, weighed and spiked with PCDD/Fs labelled standards.

After an acid/base partitioning a further purification was performed according to EPA Method 1613 Rev. B[3] by means of the automatic Power-Prep system (Fluid Management System), provided with three different pre-packed columns (multilayer silica, alumina and carbon). The eluate containing PCDD/PCDF congeners was dried under nitrogen stream and the remainder was dissolved in nonane and added of the recovery standards.

All samples were analysed by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS); the mass spectrometer was operated with EI ionisation in the selected ion monitoring (SIM) mode at a resolution of 10000. The HRGC/HRMS system consisted of a ThermoFinnigan MAT 95XL spectrometer coupled to a ThermoQuest Trace Series 2000 gas chromatograph.

The separation of the seventeen PCDD/PCDF isomers was carried out on a DB-5 MS capillary column (60 m, 0.25 mm i.d., 0.1 μm film thickness, J&W Scientific). Quantification of the seventeen 2,3,7,8 chlorine-substituted dioxins/furans was accomplished by isotope dilution method. TEQ values were calculated using WHO-TEFs[4]. Furthermore, data were also calculated as I-TEQ, using I-TEFs (NATO/CCMS)[5] in order to compare the obtained data with those referred to the previous survey[2].

Results and discussion

The total number of samples analysed for dioxins in 2001 NRSP (250) similar to that of 1999-2000 NRSP (248) and the application of the same sampling and analytical procedures make possible a critical comparison of data.

Table 2 presents toxic equivalents values (pg WHO-TEQ/g fat) with reference to the different kinds of food and feeding-stuffs, while Table 3 shows PCDD/Fs concentration (pg/g fat).

Generally, a decrease of the PCDD/Fs level in the 2001 NRSP with respect to the prior survey[2] has been observed in the matrices under investigation except for the animal feeds group, not including feeding-stuffs for fish (see Figure 1).

Among the analysed samples, two sheep's milk (4.95 and 6.15 pg WHO-TEQ/g fat) and one pig fat (13.33 pg WHO-TEQ/g fat) exceeded the European Union tolerance limit (3 pg WHO-TEQ/g fat and 1 pg WHO-TEQ/g fat, respectively)[6].

It is worthy to point out the marked difference between the mean and median WHO-TEQ values for all matrices, apart from feeding-stuffs for fish, to be ascribed to a small number of samples with a relatively high contamination level.

The highest dioxins concentrations have been found in feeding-stuffs for fish and in fish samples with levels similar to those presented in recent papers[7,8]. Their congeners patterns show that 2,3,7,8-TCDF was the predominant congener followed by the 2,3,4,7,8-PeCDF. Moreover the analysis of this data seems to indicate that dioxins/furans carry-over from feed to fish preferentially occurs for homologues with low chlorination degree.

The mean levels of dioxins detected in milk and meat samples are comparable to those reported in the literature[9,10,11]. Egg was the less contaminated food item (mean 0.24 pg WHO-TEQ/g fat) and this data is in the range or below those reported in other European countries[10,12,13].

References

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Table 1: description of examined samples

	Total	Pig	Bovine	Poultry	Sheep	Sea fish	Trout	Eel	Feed
Fish	39					12	23	4	
Fish feed	12								12
Other feeds	40								40
Egg	21			21					
Meat	82	38	23	20	1				
Fat	19	7	4	8					
Cow's milk	32		32						
Sheep's milk	5				5				
Total	250								

Table 2: PCDD/Fs levels (pg WHO-TEQ/g fat)* in food and feed samples

	Mean	Median	Minimum	90 Percentile	95 Percentile	Maximum
Fish	5.85	3.91	0.15	13.70	16.06	21.98
Feeding stuffs for fish	4.76	4.23	0.13	8.35	8.85	9.37
Animal feeds (other species)	1.19	0.49	0.07	3.15	3.69	4.14
Egg	0.24	0.08	0.05	0.61	0.62	0.70
Meat	0.57	0.20	0.04	0.87	1.28	13.33
Fat	0.52	0.21	0.06	1.08	1.27	1.74
Cow's milk	0.61	0.35	0.05	1.07	1.36	2.88
Sheep's milk	2.39	0.58	0.13	5.67	5.91	6.15

* Upper bound concentrations

Table 3: average PCDD/Fs concentrations (pg/g fat, upper bound concentrations) in food and feed samples

	Fish	Feeding stuffs for fish	Animal feeds (other species)	Cow's milk	Sheep's milk	Meat	Fat	Egg
2,3,7,8-TCDF	13.54	11.68	0.92	0.03	0.16	0.31	1.11	0.11
2,3,7,8-TCDD	0.61	0.29	0.10	0.05	0.37	0.06	0.06	0.05
1,2,3,7,8-PeCDF	1.73	1.42	0.29	0.03	0.03	0.06	0.02	0.04
2,3,4,7,8-PeCDF	5.04	4.70	0.67	0.46	1.86	0.41	0.32	0.06
1,2,3,7,8-PeCDD	0.98	0.54	0.20	0.13	0.77	0.08	0.07	0.07
1,2,3,4,7,8-HxCDF	0.67	1.07	0.98	0.46	1.09	0.43	0.23	0.09
1,2,3,6,7,8-HxCDF	0.55	0.40	0.85	0.41	0.49	0.35	0.31	0.08
2,3,4,6,7,8-HxCDF	0.78	0.89	0.58	0.21	0.36	0.41	0.16	0.24
1,2,3,7,8,9-HxCDF	0.25	0.15	0.34	0.13	0.16	0.21	0.13	0.12
1,2,3,4,7,8-HxCDD	0.21	0.15	0.23	0.10	0.18	0.11	0.06	0.04
1,2,3,6,7,8-HxCDD	0.34	0.43	0.30	0.31	0.59	0.11	0.08	0.04
1,2,3,7,8,9-HxCDD	0.13	0.11	0.27	0.06	0.03	0.08	0.07	0.03
1,2,3,4,6,7,8-HpCDF	0.20	0.33	2.42	0.13	0.20	0.37	0.09	0.08
1,2,3,4,7,8,9-HpCDF	0.07	0.05	0.18	0.05	0.02	0.07	0.07	0.03
1,2,3,4,6,7,8-HpCDD	0.84	2.09	5.73	1.39	0.60	0.86	0.49	0.50
OCDF	1.47	0.33	3.67	0.32	0.10	0.13	0.32	0.06
OCDD	1.21	5.78	43.41	1.94	0.33	1.65	1.26	1.31

Figure 1: PCDD/Fs levels (pg I-TEQ/g fat, medium bound concentrations) comparison between 2001 and 1999-2000 National Residues Surveillance Plan